SCIENCE REQUIREMENTS DOCUMENT

Binary Colloid Alloy Test – 3 (BCAT-3)

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Version.1.0.4, August 1, 2003

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1. Executive Summary

1.1. Description of Experiment

The goals of this International Space Station (ISS) bench top experiment (launched via a Russian rocket) are threefold: (1) to optimize the selection of viable samples for use in the Light Microscopy Module (LMM) that is scheduled to fly aboard the ISS starting in 2006, (2) to further investigate critical, fundamental problems in colloid science, (3) and to evolve the field of "colloid engineering", which creates materials with novel properties using colloidal particles as precursors. In these cases, gravity-driven sedimentation and convection precludes these experiments from being carried out on earth, and requires a microgravity environment to address many of the most critical questions.

This experiment is envisioned as a direct follow-on to the Physics of Colloids in Space (PCS), Binary Colloid Alloy Test (BCAT, BCAT-2), and Colloidal Gelation (CGel) flight experiments. This bench top experiment will provide science results and optimize sample selection for PCS-2 and the Low Volume Fraction Entropically Driven Colloidal Assembly (LΦCA) experiments, which are currently scheduled to fly in the Light Microscopy Module (LMM) aboard the ISS starting in 2006.

This experiment will focus on up to four classes of colloidal samples (depending upon the final samples selected):

The first set of samples described is binary alloys. These contain a mixture of two different colloidal particles suspended in a fluid. If the size ratio, r, and volume fraction, ϕ, are adjusted appropriately, the particles will self-assemble into ordered binary alloy crystal structures. In BCAT-3, by varying the amounts and types of materials in the colloids, crystals will be created and examined, which will facilitate a better understanding of the mechanisms at work. Different ratios of particles of different types should provide phase diagram shifts, which may show up as different color bands in the photographs of samples that have crystallized. So the BCAT-3 bench top experiment will provide a qualitative determination of which samples crystallize in a microgravity environment and hence which samples most merit consideration for use in PCS-2.

The second set of samples described will be a mixture of colloidal particles with polymers. The addition of the polymers induces a controllable attractive force, due to depletion, between the colloidal particles. This attractive force facilitates the formation of other structures. In addition, the presence of an attractive force induces new phase behavior in the colloidal suspensions. The ratio of colloidal particles with polymers flown on PCS produced spinodal decomposition, but the samples flown did not reach critical opalescence. BCAT-3 will allow the particle size ratio and volume fraction to be determined for reaching the critical point of the colloidal polymer (col-pol) solution, thus allowing PCS+ to make a quantitative characterization of these important processes.

The third set of samples described will be a mixture of entropically driven low-volume fraction colloidal particles, which are reasonably well approximated as a suspended mixture of hard-spheres. These will be suspended in an index matching mixture of decaline and tetralin and will form surface crystals. The samples are made from tightly controlled volume fractions of large (~ micron sized) particles and small (~ 0.1 micron sized) particles in the decalin/tetralin background fluid. The reason surface crystals grow is because when the large particles pack next to each other they free up more volume for the small particles. The increased number of configurations in the added volume for the small particles increases their entropy more than the large particles loose due to packing. Hence, entropy drives the crystallization. Surface growth is favored because large particles packing next to the wall free more volume for small particles than two large particles touching out in the bulk.

The merit of low-g here (over 1-g) is the modest reduction of the chemical potential gradient in the sample due to gravitational potential variation with height. If PMMA is ~ 0.9 g/cc and decalin/tetralin is ~ 1.07 g/cc, then sedimentation is slowed in low-g. When a cuvette grows successfully a human should see a filmy nature to the glass surfaces of the cuvettes. If the crystals grow thick (tens of layers), then there will be some color variation with angle when viewing transmitted (back-lit) light. This is not unlike the bulk crystals of PMMA seen in previous colloid experiments in space.

The forth set of samples will consist of colloidal particles that are all 271 nm in diameter, that is, 0.271 microns, (with a 10 nm PHSA stabilizer coating). These samples from the forth set will have two sample cells, each with a different volume fraction in the glassy regime, one being 61.5 volume percent and the other being 62.5 volume percent in concentration for PMMA particles in a decalin/tetralin index matching solvent. The samples will be homogenized initially, and then we will observe crystal structure evolution using a camera.

Because of the qualitative nature of the BCAT-3 bench top experiment, BCAT-3 will be useful in determining when samples crystallize or are at a critical point in a reduced gravity environment, and hence which samples merit consideration for the LΦCA and PCS-2 flight experiments.

1.2. Scientific Knowledge to be Gained

These experiments will provide a unique example of the use of colloid engineering to synthesize new materials with novel properties. The goal is to exploit the long range ordered structures formed using the self-assembly of colloidal particles. The use of mixtures of two different materials greatly increases the flexibility of the resultant structures; for example, the characteristic length scale of the structure can be set by one material, which could be an inert plastic, while the second material could have some completely different property, and could, for example, be an optically active semiconductor particle. This provides an opportunity to synthesize structures that are ordered on the length scale of light in all three dimensions, and such materials should have fascinating new properties. For example, they may be suitable for optical switches or filters, or as photonic band gap materials. Fabrication of 3D ordered structures with

traditional lithographic methods is very difficult, and has not been done on the optical length scale; the use of colloidal materials allows the structures to be self-assembled, providing a new method for materials synthesis. In addition, we will qualitatively study the phase behavior and crystallization properties of these binary alloys. This will provide additional insight into their growth allowing us to further tailor the crystal structure.

We will also study the properties of mixtures of colloids and polymers where the addition of the polymer induces weak attractive interactions between the colloidal particles by the depletion mechanism, leading to a rich phase behavior for the colloidal particles. We will focus on the behavior near coexistence regions, where two or three phases exist simultaneously in the sample. We will study the structure and behavior of these phases, addressing critical questions that have been obscured in previous studies because of limitations imposed by sedimentation.

The crystallization of glasses is one of the most fundamental and significant problems in soft condensed matter physics today. This surprising phenomena, which occurs in reduced gravity in days to weeks, seems to take geological time scales to occur on earth. Having bulk samples of significant size to repeat this observation, first seen in the CDOT flight experiment, should lend addition insight and credence to this finding.

1.3.   Value of Knowledge to Scientific Field

Although there has been considerable interest in the use of self-assembly for new routes of materials synthesis, relatively little has been done with colloidal particles as precursors. The use of binary alloys is a promising method to obtain additional flexibility in the design of new materials; however it has not been extensively explored. One of the main impediments in its use is the problem of differential sedimentation of the colloidal particles if the two types have different densities; this restricts most studies to particles of the same material, but of different sizes. These studies will be the first to explore this exciting and promising form of colloid engineering, by using particles that have both different sizes and are made of different materials.

The study of weakly attractive interactions between colloidal particles has mainly focused on their phase behavior. However, this work has generally been restricted to measuring the relative quantities of the different phases that are formed; thus we have not taken full advantage of the colloidal scale of the particles, which should allow much more information to be learned about the nature of the formation of these phases. Much of the impediment for this has been the gravity-induced sedimentation. While this is essential for determining the relative quantities of each phase formed, and hence the phase diagram, it also obscures any study of the structures of the different phases. Thus these experiments offer the first opportunity to measure the behavior of these systems. In addition, this attractive interaction will be used in the formation of new materials with colloidal particles as precursors.

The experiments push the boundaries of known self-assembly and thermodynamics processes in complex fluids. Clean observations of phase transitions in more complex systems consisting of particles whose direct interactions are beyond hard-

sphere, provide much needed insight about the interplay of particle interactions, polydispersity and sedimentation in affecting phase behavior. These effects are normally masked in experiments on earth. Clean observations, for example, about how the liquidous lines are perturbed by particle non-ideality reveal trends that are broadly useful in suspension science – trends that should improve design criteria for control of soft materials ranging from protein crystallization to paints. Careful studies of colloidal epitaxy with templates in microgravity will break new ground about the possibilities for growth of closed-packed, open and exotic colloidal structures. Traditional questions about the relative stability of BCC and FCC phases, and the passing from one phase to the other, can be studied in the simplest of systems with exquisite resolution without the perturbing effects of sedimentation. Disorder can also be induced by the surface templates, so that new questions about glass formation can be studied in microgravity. The nature of nucleation and the configurations of the solid-liquid (and solid-solid) interface are poorly understood, and the current experiments provide new windows into these processes.

1.4. Justification of the Need for a Space Environment

The formation of colloidal crystals is strongly affected by sedimentation; this is most graphically demonstrated by the results of the experiments of Chaikin and Russel, who showed that the morphology of colloidal crystals grown in space is completely different from that grown on earth. The primary reason for this is sedimentation. As the crystals sediment, the shear of the fluid flowing past their edges is sufficient to destroy them. In addition, the sedimentation time of the crystals rapidly begins to compete with the diffusion time of the accreting particles, significantly changing the growth mechanism. While some of this effect can be mitigated by buoyancy matching, this is not completely effective, even at the best level of buoyancy match that can be achieved. By contrast, performing the experiments in microgravity significantly reduces the sedimentation, and eliminates the problems. Thus very large crystals can only be grown in microgravity. This is essential both to study the very delicate structures of the colloid-polymer mixtures, and to allow the binary alloy colloidal crystals to grow. In addition, when colloidal particles of different materials are used, it is even more essential to perform the experiments in microgravity; otherwise the differential sedimentation of the different particles will prevent growth of any crystals.

2. Background

2.1. Current Application for Research

The primary goal of PCS-1 is to develop the basic principles for synthesizing several different sorts of materials, to determine the fundamental properties of the growth of these materials, and to begin the study of their basic properties. PCS-2 will continue this program, building on the results of PCS-1. However, the primary goal will be to more fully develop colloid engineering, to synthesize new materials, and to more fully characterize their properties. The type of materials that will be studied in PCS-2 will be broader than in PCS-1, allowing a more complete suite of materials to be synthesized. In

addition, the nature of the experiments that will be performed will be significantly different. As a result, the equipment required differs from that required for PCS-1.

In PCS-1, three classes of colloidal materials will be studied. These include ordered crystalline samples; mixtures of colloidal particles with other species, primarily polymers, which induce a weak attractive interaction allowing us to precisely tune the phase behavior of the mixtures; and highly disordered, but very tenuous fractal structures which possess their own unique symmetries and their own unique properties. In PCS-2, we will emphasize materials synthesis, and will extend the range of materials used. In addition, we will study the structure and dynamics of these systems in real space, allowing us to probe local structure in unprecedented detail.

2.1.1. Binary Alloy Crystals

In PCS-1, we will study the formation of binary colloid alloys made of a single material, poly-methylmethacrylate, or PMMA. This will allow us to nearly index match the colloids to the surrounding fluid and to use the full slate of light scattering analysis tools available to the PCS-1 apparatus. The goal of the PCS-1 experiment will be to develop a better understanding of the fundamental crystallization mechanisms that control the crystal growth, and to explore the properties of the alloys.

In PCS-2, we will exploit the knowledge gained from PCS-1, as well as all the other flight and ground based experiments we have conducted. We will focus on making new binary alloy crystals comprised of colloidal particles of different materials. The goal will be to synthesize structures that have interesting optical properties. Many of these properties arise because the periodicity of their lattice constants of the crystals is on the same scale as the wavelength of light; this scale is set by the choice of particle size. Because their structure is periodic, binary alloy crystals diffract light. However, the diffraction is not limited to a single direction, as is, for example, a simple grating, but can instead potentially be in all three directions simultaneously. Because of the 3D structure, the fabrication of these diffraction gratings with traditional lithographic techniques is extremely difficult. By contrast, the self-assembly of colloidal particles may make it much simpler.

In PCS-2, we will likely still use PMMA particles as one of the colloids; they are well understood, and provide a useful space-setting material; they are optically inert, and can be synthesized in very monodisperse suspensions with finely controlled sizes. The second colloidal particles will probably be either metallic particles, which will be useful for the purpose of making optical filters, or semi-conductor particles, which will be useful for making optically active materials. In addition, we may use tertiary mixtures wherein the smaller particles are composed of mixtures of PMMA particles and a small fraction of the optically active particles, to allow us to dope the binary structure with only a small fraction of the optically active material. We also plan to use other materials to achieve different properties for the final structures. We plan to use particles that contain a liquid crystal within them. The optical properties of the liquid crystal can be significantly modified by the application of an external electric field, allowing an additional degree of control over the properties.

While many studies of the PMMA binary alloys can be carried out in our ground based research program, relatively little work will be possible with most of these mixtures of different materials. The key problem is the difference in the densities between the two particles. This makes it intrinsically impossible to buoyancy match the particles, as only one of the species can be buoyancy matched. As a result, many of the initial measurements will have to be carried out in microgravity. Our earlier studies will have identified the optimal phase space for formation of binary alloy crystals from PMMA, in terms of the optimal particle size ratios and volume fractions for a given structure. However, because the particles will be of different materials, the interparticle interactions will most likely be slightly different, requiring a somewhat larger steric stabilization of the particles. This may result in a slight modification of the interactions, changing the phase behavior. As a result, we will need to deploy a wider range of samples in the microgravity experiments to allow us to extend the boundaries of the phase space explored.

2.1.2. Colloid-Polymer Mixtures

In PCS-1, we will explore the bulk properties of samples of attractive particles, using the scattering tools available in the apparatus. This will enable us to follow the dynamics of the phase separation after homogenization, and will probe the kinetics of the formation of the different phases. This will provide important macroscopic information about the nature of the phase transitions. However, this will leave many crucial questions unanswered. Since the sample size will be relatively large, the light beams will probe an extended region of the sample, inevitably measuring a mixture of phases, and precluding the investigation of any individual phase. In PCS-2, we will have the facilities to probe very small sample volumes and to measure the behavior of isolated regions within these samples, allowing us to measure the properties of only single phases.
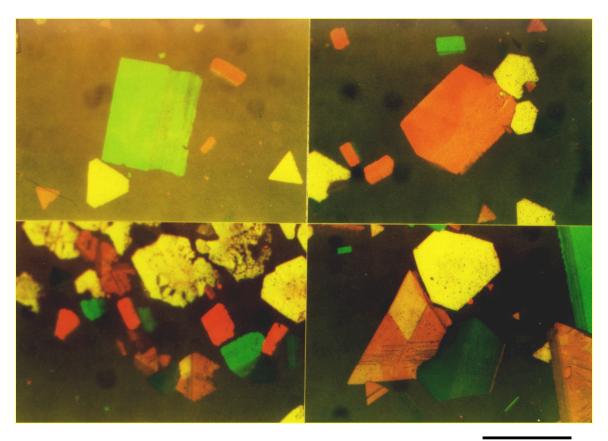
Among the key issues we will address is exactly how the phase separation proceeds. For example, when three phases coexist, we will investigate the mechanism for the formation of crystals, to determine whether the system first separates into a gas and fluid with the fluid further separating into a liquid and solid. If this is the case, then the crystals are formed in the fluid phase. Alternatively, some solid may sublime directly from the gas phase, while the remainder comes from the fluid phase. We will also investigate the nature of the droplets of liquid as they form, and will determine the surface tension of these droplets by studying their fluctuations. The surface tension should be extremely small and such an effect has never been determined in ground based measurements because of the low magnitude. However it should be possible in PCS-2.

We will also investigate the nature of the crystal structures formed by the depletion attraction. When monodisperse particles crystallize through entropic hard sphere repulsive interactions, there is apparently very little energetic difference between two close packed structures, face centered cubic (FCC), and hexagonal close packed (HCP). As a result, the structure formed is a mixture between the two, a random stacking of hexagonal close packed planes (RHCP). By contrast, the structure of attractive particles is still not well determined. However, it is quite conceivable that with an attractive interaction, one structure will be preferred over others. This would be very

useful for colloid engineering; RHCP structures are strictly speaking not true crystals at all, as they lack long range order in all directions. As a result, they exhibit Bragg rods rather than Bragg points in *q*-space, which would be deleterious to their use in any photonic structure. Thus we will explore whether it is possible to create more highly ordered structures by means of an attractive interaction.

2.1.3. Low volume fraction colloidal crystal growth using novel materials

The type of particle flown for the low volume fraction colloidal crystal growth studies consists of polymer-based spheres such as PMMA, polystyrene (PS). These particles must be stable against aggregation in their solvent.

Figure 5: Wall crystals formed by entropic forces.
A. Yodh sample, front-illuminated.

500μm

2.2.   Anticipated Advance in the State of the Art

Addressing the questions proposed above would significantly increase our understanding of the properties and behavior of colloidal suspensions. In addition, they would provide crucial guidance in the use of colloidal precursors for materials synthesis, and would help establish colloid engineering as a new synthesis route. The materials produced would all have unusual properties, that have not yet been fully anticipated.

3. Justification for Conducting the Experiment in Space

3.1. Limitations of Ground-Based Testing

The primary limitation with ground-based work results from sedimentation. A second less critical problem arises due to convection effects, which are also gravity induced. Both of these effects will be greatly reduced in microgravity. A basic understanding of the limitations imposed by gravity comes from the problems encountered in current experiments. We review these first, and then discuss more detailed estimates of the effects of gravity, even in the optimum case.

Experiments in Edinburgh probe the formation and structure of crystals from monodisperse colloidal particles using microscopy. They use small capillary tubes as sample cells; these are about 2 mm wide and about 100 μm thick. These samples are loaded in a fluid state, the cell is sealed and the measurements begun. In the course of about an hour, the samples crystallize. The crystallization process is studied and the final structures are determined by imaging. However, during the course of the experiment, it is inevitably noticed that the particles sediment, so that the top of the cell has a lower density, which typically remains fluid, while the bottom has a higher density, where the crystals form. Thus, it is impossible to accurately set the volume fraction. Moreover, the sample at the bottom is always under the additional osmotic pressure of the sample above; this has a direct effect on its properties. In addition, as shown by the results of the CDOT experiment by Chaikin and Russel, the morphology of the crystals is significantly modified by the gravity-induced settling. This limits the size of the crystals that grow, which will place a significant limitation on their use for materials growth.

Experiments conducted by Segre at Penn and at Harvard also highlight the effects of gravity. He used time lapse video to record the formation and growth of the crystals from larger scale samples, again of monodisperse particles. He first used the standard mixture of index-matching fluids, tetralin and decalin, for which there is a density mismatch of $\Delta\rho \approx 0.25$. He observed the crystals to sediment quite rapidly. He then repeated the experiment using cycloheptyl bromide, which can be used to achieve a more nearly buoyancy matched sample while still index matching the PMMA. He estimated that the density mismatch was decreased by about two orders of magnitude, to $\Delta\rho \approx 0.002$ (this is probably an optimistic estimate, with the actual density match being poorer); however, while the sedimentation velocity was reduced, and the crystals were larger and more dendritic, they also clearly continued to sediment. Because of uncertainties in mixing volumes, it is unlikely that density matching closer than this can be achieved; differences in thermal expansions also limit the exact buoyancy match. In addition, the only way to reliably and accurately set the volume fraction of the samples is to take advantage of their phase behavior. Their volume faction can be adjusted to be in the two-phase region, with ϕ between 0.5 and 0.55, where both the fluid and crystal coexist. The fluid has $\phi = 0.5$, while the solid has $\phi = 0.55$; by allowing the denser crystals to sediment to the bottom of the sample, the volume fraction of the supernatant fluid is set exactly at $\phi = 0.5$. Accurate adjustment of the volume fraction is essential for

all experiments, and this is the only reliable and accurate way of doing this. Thus, even the slow sedimentation of the buoyancy matched samples is highly desirable.

A final observation about gravity induced effects comes from some of the results obtained in the CGel glovebox experiment. In this experiment, samples remained in microgravity for about 4 months, when they were photographed. Although the results are not entirely certain, since no light scattering was performed, some of the pictures seem to show a noticeable difference in apparent photographic density from the top to the bottom of the cell. While it is not entirely certain, one explanation for this observation is that the material had sedimented slightly during the course of the experiment. Thus, it may actually be desirable to use as close to buoyancy matched particles as are available in the microgravity experiments to minimize this effect for the most delicate of samples and the longest duration experiments.

For BCAT-3, the experiments where sedimentation effects will be most critical and the experiments will have the longest duration are probably the colloid-polymer mixtures. For these samples, the structure formed, particularly the liquid droplets, will be most susceptible to sedimentation. In particular, studies of their shape fluctuations to measure the effective surface tension will demand that there are no other effects that dominate, and will require very precise buoyancy matching. By contrast, the binary alloy colloidal crystals will not be able to be matched at all, and will absolutely depend on microgravity to form. However, our experience with the glovebox experiments has already shown that we are able to form good AB_{13} crystals from PMMA in microgravity, making it highly likely that we will be able to reproduce this using the new materials proposed here.

We can make several estimates of the effects of gravity on the crystals. The first one is to calculate when sedimentation can compete with diffusion for the growth of the crystals. The concept here is that a free crystal grows by diffusion of the accreting particles to the surface. Competing with this is the sedimentation of the whole crystal. We can estimate an effective Peclet number, Pe_{eff}, which expresses the ratio of the time for a single particle to diffuse its own size, t_D, to the time for the crystal to sediment a single particle size, t_C. We might expect that when $Pe_{eff} = t_D/t_C \sim 1$, the effects of sedimentation will become significant. This will allow us to estimate a maximum crystal size that can be achieved. We do this for crystals from monodisperse particles as all the required parameters are known for them.

The buoyant mass of a crystal of typical radius R_C is given by

$$m_b = 8 \, \Delta\rho_p \, \Delta\rho \, R_c^3 \qquad (1)$$

where $\Delta\rho_p = 0.05$ is the difference in particle density between the crystal and the fluid, while $\Delta\rho$ is the intrinsic difference in density between the particles and the surrounding fluid. The sedimentation velocity can then be calculated by balancing the gravitational force on the crystal with the Stokes drag of the fluid, resulting in

$$v_C = \frac{\Delta\rho_p \; \Delta\rho \; g \; R_C^2}{6\,\pi\,\eta} \qquad (2)$$

where g is the gravitational acceleration constant and η is the viscosity of the surrounding fluid, which we take to be the value of the viscosity of the fluid phase which is about 50 times that of the solvent. The characteristic times are then

$$t_C = \frac{R}{v_C} \qquad (3)$$

and

$$t_D = \frac{R^2}{D} \qquad (4)$$

where D is the diffusion coefficient of the single particles, which we calculate using the Stokes-Einstein relation,

$$D = \frac{k_B \; T}{6\,\pi\,\eta\,R} \qquad (5)$$

where T is the temperature and k_B is Boltzmann's constant. This allows us to calculate the effective Peclet number for this form of crystal growth,

$$Pe_{eff} = \frac{8\,\Delta\rho_p \; \Delta\rho \; R_C^2 \; R^2 g}{k_B \; T} \; . \qquad (6)$$

If we use $P_{eff} = 1$ as a criterion for when sedimentation becomes important, we can determine the maximum crystal size that can grow under different conditions,

$$R_{C,\max} = \sqrt{\frac{k_B \; T}{8\,\Delta\rho_p \; \Delta\rho \; g \; R^2}} \approx \frac{3\mathrm{x}10^{-7}}{\sqrt{\Delta\rho \; g \; R}}\,\mathrm{cm} \qquad (7)$$

using CGS units. If we use $R = 0.5$ μm, we can calculate the size of PMMA crystals that can be formed on earth with the standard index matching solvents, decalin and tetralin, for which $\Delta\rho \approx 0.25$ gm/cc and $g \approx 10^3$cm/sec^2. We obtain a value of $R_{C,\max} \sim 4$ μm; this is consistent with the observation that dendritic crystals are never observed on earth. The value of $R_{C,\max}$ varies inversely as the square root of both g and $\Delta\rho$, allowing us to estimate the effects of both buoyancy matching in microgravity. If we improve the buoyancy match by two orders of magnitude, the size of the crystals will increase by one order of magnitude to $R_{C,\max} \sim 40$ μm. By comparison, using the standard non-buoyancy matched fluids, but doing the experiment in microgravity adds an additional 3 decades, to crystals of about $R_{C,\max} \sim 4$ mm, again consistent with what is seen in the CDOT

experiments. Combining the approaches of near buoyancy matching and microgravity will produce crystals of remarkable sizes, $R_{C,\max} \sim 4$ cm!

Of course, these are the simplest cases to consider. However, it also gives us guidance for the binary alloys. The key is the square root dependence on both $\Delta\rho$ and g. Thus even a far less favorable density mismatch of 20 would decrease the size of the crystals by a factor of 10, while microgravity would still provide a benefit of three decades. As a result, we might estimate $R_{C,\max} \sim 400$ μm in the most unfavorable case of binary alloys with a large density mismatch, provided we do the experiment in microgravity. This size is still quite reasonable for making materials with interesting optical properties.

Finally, it also interesting to estimate the actual sedimentation velocity for some cases. It is given by Eq. (2), and for a 100 μm crystal of PMMA in decalin and tetralin in microgravity, $v_C \sim 0.5$ μm/sec on earth, where we have assumed that $\eta = 1$ Poise. In microgravity, this is reduced by six decades, becoming more like about $v_C \sim 1$ μm/month. For binary alloy colloidal crystals, this value might increase to several μm/month. This should be tolerable in performing these experiments.

In evaluating the significance of these calculations, we feel that the estimates for the monodisperse PMMA crystals are probably more relevant to the glassy PMMA and colloid-polymer mixtures, while estimates for the binary alloys should use the large density mismatch calculations above. The exact value of the density mismatch will depend on the materials chosen; however representative values are: silica; $\Delta\rho \cup 1.3$ gm/cc and gold; $\Delta\rho \cup 17$ gm/cc and these values were used above.

3.2. Limitations of Drop Towers

The length of time for formation of any of these structures is far too long for short term microgravity experiments, such as those performed in a drop tower or in an airplane. In a drop tower, low gravity is achieved only for a few second. The growth of binary colloid alloy crystals can take weeks to months on earth; it may be more rapid in microgravity, but will still take several weeks. Similarly, the phase separation of colloid-polymer mixtures can take several minutes to many days. It also is much to slow for the parabolic loop of an airplane.

3.3. Limitations of Testing in Aircraft

The length of time for formation of any of these structures is far too long for short term microgravity experiments, such as those performed in a drop tower or in an airplane. In an airplane, low gravity is only achieved for less than a minute. The growth of binary colloid alloy crystals can take weeks to months on earth; it may be more rapid in microgravity, but will still take several weeks. Similarly, the phase separation of colloid-polymer mixtures can take several minutes to many days. It also is much to slow for a drop tower of an airplane. Glassy volume fractions of PMMA spheres in an index

matching fluids sit for geological timescales on earth without crystallizing and crystallize within weeks in reduced gravity (probably due to the lack of gravity induced jamming).

3.4. Need for Accommodations on the Space Station

The space station provides an environment where microgravity is sustained long enough to allow these experiments to be conducted. The samples can be homogenized by mixing them and then can be allowed to develop under microgravity for an extended period of time. Their structure and properties can then be probed in situ allowing the unique behavior of the new materials to be studied.

3.5. Limitations of Mathematical Modeling

The phase behavior of binary alloy colloidal crystals has been calculated, primarily using maximum packing considerations. However, while these calculations are a useful guide for experiment, they tend not to be in direct agreement with the experimental results. Thus, further experiment will provide additional guidance for further refinement of the theory.

Theoretical calculations of the optical properties of a variety of structures have also been calculated. However, these calculations are quite difficult and can not be done analytically. As a result, they tend to focus on structures that can be easily fabricated, and have not, as yet, been performed for binary alloy colloidal crystals. While these would be useful, they are not essential for performing the experiments. The experimental results obtained should be very helpful in directing any future modeling. They will provide the essential experimental input that is critical to test new models.

3.6. Limitations of Other Modeling Approaches

Other modeling is rudimentary or non-existent. The experiments proposed here will provide the definitive data to allow further modeling to be carried out.

4. Experimental Details

4.1. Experiment Procedures to be Used for BCAT-3

4.1.1. Binary Alloy Colloidal Crystals

The samples will consist of polymethylmethacrylate (PMMA) particles, stabilized by a thin coating of poly-12-hydroxystearic acid. The solvent will be a mixture of decalin and tetralin and possibly other chemicals to exactly match the index of refraction of the PMMA. The choice of the size ratio, particle concentration ratio and total particle volume fraction will be based on the results of the preliminary glovebox experiments and ground-based investigations of the phase diagram, supplemented by the results of PCS-1. Once in orbit, the samples will be homogenized by shear melting with a magnetic stir bar.

Once the sample is homogenized, the nucleation and growth of individual crystallites of the binary colloidal alloy will be monitored with photography. Compared to the growth of monodisperse crystals the growth process in binary systems is likely to differ because the two particle species have to be ordered on the surface of the crystal.

4.1.2. *Colloid-Polymer Mixtures*

The colloidal particles for this experiment will again be PMMA spheres suspended in an index matched fluid. The volume fractions of these samples will range from about 1% to 30%. The polymer will be polystyrene, with a molecular weight ranging from about 100,000 to 1,000,000.

The colloid-polymer mixtures will be homogenized using the same procedure used for the binary colloid mixtures. After they are homogenized, the formation of the gel will be monitored by taking 3D stacks of images in the same way as for the binary colloidal crystals.

Colloidal crystals may form in one of the phases. Since they can form at low volume fractions and result from an attractive interaction between the particles, their growth and evolution may be significantly different from the formation of those formed by hard spheres. We will use photography to study their evolution in a way that is analogous to the one described in the section above about binary colloidal crystals.

4.1.3. *Low volume fraction colloidal crystal growth using novel materials*

The same decalin/tetralin system used by Weitz and same particles used for the binaries listed above, with added polystyrene polymer.

4.1.4. *Colloidal crystal growth of glasses*

The PMMA particles we used were ASM74 (particles synthesized by A. Schofield in Edingburgh). ASM74 has the following physical properties:

unswollen diameter = 249 nm
swollen diamter = 271 nm
PHSA layer = 10nm
density (unswollen) = 1.19g/cm^3

All particles suspensions are formulated to be 55% tetralin after swelling (the remaining solvent being decalin). All become index matched (clear) once equilibrated by placing in an oven at 80C for two hours (or for 50C over the weekend). Before equilibration, the suspensions are milky white, indicating an index mismatch, but much less viscous and hence much easier to put into a sample cell. Upon transferring, the samples are remixed using a touch mixture, to mitigate any affects of settling. There are approximately 2.5 mL of each sample in the flight cells.

4.2.   Measurements Required

4.2.1.   Binary Alloy Colloidal Crystals

Nucleation and growth:
-        Homogenization by strong shearing
-        Time series of 2D camera images
Structure determination:
-        Time series of 2D camera images

4.2.2.   Colloid-Polymer Mixtures

Growth of gel-like structure:
-        Homogenization by strong shearing
-        Time series of 2D camera images

Properties of gel-like structure:
-        Time series of 2D camera images

Equilibration of gel-like structure:
-        Time series of 2D camera images

4.2.3.   Low volume fraction colloidal crystal growth using novel materials

Nucleation and growth:
-        Homogenization by strong shearing
-        Time series of 2D camera images

4.2.4.   Colloidal crystal growth of glasses

Nucleation and growth:
-        Homogenization by strong shearing
-        Time series of 2D camera images

4.3.   Test Plan including Ground Characterization of Flight Hardware

Ground based experiments are currently underway to support PCS-2 as well as PCS-3. For the binary colloidal crystal alloys, we have fabricated a supply of PMMA particles, that can be dyed for experiments using fluorescence microscopy.   Also, experiments with systems containing liquid crystal droplets are underway. Their phase behavior should be similar to that of PMMA, although this will be tested to determine any differences. However, their optical properties can be controlled by an externally applied electric field which will align the liquid crystal molecules in the droplets and change their scattering properties. Other potential new particles will also be explored.

Experiments now underway in the laboratory will provide a data base on imaging of various types of samples with confocal and video microscopy (monodisperse and binary PMMA samples, PMMA-polymer samples, liquid crystal droplets). PCS-1, followed by BCAT-3 and additional ground-based experiments will show which particle

diameter ratios and volume fractions for the various sample types will be most promising for the colloidal engineering experiments of PCS-2. Also, experiments using laser tweezers for rheology, modification of crystal lattices and pattern formation are planned.

To ensure that the optimum information can be obtained from the space experiment, it will be essential to have a model of the apparatus available to the PI's. This will allow testing of the experimental procedure and will enable the PI's to learn all the inevitable idiosyncrasies of the apparatus. The apparatus should be available to the PI's while it is being constructed at GRC. This will significantly ease the burden of software development for the GRC team. In particular, considerable development of confocal microscope software and analysis has already been done at Harvard University, however it was done with a different confocal microscope. However, if a model of the flight system is available at Harvard University, many of the analysis routines can be adapted directly to the NASA system. This can happen only if there is flight-like hardware at Harvard University. This would significantly improve the chances of success for this experiment.

4.4. Specific Analysis Required

Major parts of the software that will be necessary for data analysis exist already and are used routinely for the data analysis of ongoing ground based experiments. In particular this includes software for image analysis and particle recognition as well as software for the recognition and structure analysis of colloidal crystals.

4.5. Preflight Experiment Planned

All experiments that are planned for PCS-2 will also be done before the flight, either with inverted microscopes or on the flight instrument. More details about preflight experiments are given in section 4.3 above.

4.6. Post Flight Data Handling and Analysis

The same form of data analysis will be used after the flight as is used during the flight. Additional software that is required for data analysis will be purchased or written by the principal investigator team.

The post-flight data analysis will require that the PI's have access to as much of the raw data collected during the flight as possible.

4.7. Mathematical Models Used

Well-accepted mathematical models representing the physics of fluid mechanics, volume fraction fluctuations, and Brownian motion will be the basis for data analysis.

The experimental results may serve as a guide for developing new mathematical models.

Analytical and numerical modeling of both the phase transition phenomena and photonic bandstructure provide significant insight, but typically employ simplifying approximations which do not reflect the true experimental realities. The experimental results should be very helpful in directing future modeling efforts, testing new models, and defining fruitful new experimental directions.

4.8.   Application of Results

The results of these experiments will increase our knowledge of the phase behavior of mixtures of colloidal particles of different types. Also, new insight into the crystal structures that are formed by alloys of colloidal particles as well as the kinetics of their growth and the dynamics and properties of the structures formed will be gained.

5. Experimental Requirements for BCAT-3

The following sections contain specific requirements necessary in order to fulfill the science mission for BCAT-3.

5.1.   Sample Description

Binary alloys and colloid-polymer samples will be used for these experiments. The PI will provide all these samples for the ground tests and flight experiments. The PI will assure sample quality, cleanliness, and suitability/compatibility for examination over the wavelength range of experimentations. More sample details are provided in Section 4 (especially Section 4.1) above.

5.1.1. Binary Alloys

5.1.2. Colloid-Polymer Mixtures

5.1.3. Low volume fraction colloidal crystal growth using novel materials

5.1.4. Colloidal crystal growth of glasses

5.2.   Sample Cell and Instrument Requirements

The sample cell and flight instrument shall have the capability for:

5.2.1. Sample Homogenization

Homogenization shall be sufficient to "melt" the colloidal sample and disperse any existing crystallization. Homogenization and photography are required within a day, a week, a month, and two months after the initial homogenization (sample mixing). Rehomogenization of individual samples will allow the study nucleation and growth and is desired, if time is available.

5.2.2. *Optical Imaging*

Visual imaging and the accompanying color pictures of individual cells and crystals (when visible) are desired. The desired depth of field and magnification is provided in the experiment procedures (and is fixed by available hardware). A temperature change of more than +/- 0.5 C should be noted when the photographs are taken. Color images are required for the determination of when samples have crystallized. For camera settings, see Optical Imaging in the Science Requirements Summary Table.

5.3. Sample Cell Requirements

In addition to the sample cell requirements described in section 5.2, the sample cells shall contain the colloidal samples during the length of the experiments, shall provide volumes from approximately 2.5 c.c.'s (e.g., roughly 10 x 10 x 53.5 mm OD, and 4 x 8 x 35 mm ID), with rectangular shaped wells (e.g., mm) (to minimize sample volume while maximizing area available for photographing). These sample cells shall provide for manipulation and optical viewing of the samples while being contained in a sample holder. It is also essential that each sample cell contain a stirbar, which can be moved by an external magnet to homogenize the sample volume at the beginning of an experimental. Ten sample cells are needed (with more desired).

5.4. Delivery Requirements

For BCAT-3, it is desired that arrangements be made for late delivery of the samples (2 months or preferably days before launch). However, we will take what we can get, with the understanding that late sample delivery requires much less effort for sample homogenization on the part of the astronaut(s).

5.5. Atmosphere Requirements

Normal pressures and temperatures of the cabin environment should suffice for the samples. For the pure solvents the temperature should remain above freezing (> -40°C preferred, successfully tested to -40°C) and below boiling (< 190°C) and such that volume changes do not damage the cells. Tests from -50°C to +50°C indicate that this temperature range required for transport to and launch aboard a Russian rocket in winter is acceptable (although not preferred).

5.6. Vibration Control and Measurement

For the instrument as a whole, the dc component of gravity is most important for this work. An experiment must be long in duration, but needs no better than 10^{-3} g; averaged over an hour. However, the samples must not be jarred after homogenization and prior to the light scattering measurements. If a crystallized sample is disturbed, its opalescence will disappear. Accelerations greater than 10^{-3} could disrupt the ordered domains. This experiment is really more sensitive to the lower frequency accelerations. The limit on acceptable average acceleration is given by: $g_{ave} = 10^{-3} (1/\tau)^{1/2}$, where g_{ave} is the allowable average acceleration, and t is the time frame of interest, expressed in units of hours. Therefore, over a one hour time frame the allowable average acceleration measured at the

sample cell is 1 mg (milli-g). Since the vibration environment cannot be controlled, measurement of the vibrational environment during the mission should provide enough information to determine if samples were disturbed during critical periods.

5.7.   Imaging Requirements

Downlinked color ccd images of the samples are needed just before and after homogenization. Color images are also required at various stages of the experiments. This will enable the PIs to examine the state of the samples to assess whether equilibration has occurred.

5.8.   Astronaut Involvement

Astronaut involvement is envisioned for setting up the experiment to be photographed.

On-Orbit Operations and Crew Time Estimate
1. Set up MWA   1 hour
2. Unstow Hardware   5 minutes
3. Homogenize Samples (to start the experiment) 10 samples x 5 minutes =50 minutes
4. Photograph Samples   10 samples x 6 minutes = 60 minutes
5. Stow Sample Module 5 minutes
6. Repeat Photography (steps 4 and 5) with the desired time of 1 day, 1 week, 1 month and 2 months after homogenization and initial photography
7. Additional photographs are desired if astronaut crew time allows (particularly within the first 48 hours after homogenization. Repeat the test after 2 months as time allows (Re-homogenize and repeat photography).

Minimum crew time = the time for steps 1-6 (one time) = 7.5 hours
Science Reserve = 42.5 hours
Crew Time: 7.5 - 50 hours (Minimum of 5 sets of photos)

Since the photograph sets can occur over a period of months, the PCMMIA cards used with the Kodak 760 cameras to acquire images will require astronaut time and involvement to downlink images. Additional downlinking requests are given in section 5.7, immediately above.

5.9.   Data Requirements

On-board data storage requirements:
- All visual images, and other such data should be time-tagged to MET, and GMT.
- Voice annotation of photographs is desired when deemed appropriate by the astronaut.
- Accelerations in excess of 10^{-3} g should be recorded and time-tagged for comparison with data from the experiment.
- All images should be stored with a record of the experimental conditions such as, when the measurement was made, length of measurement, if and how lighting conditions have changed.

- Temperature is to be recorded whenever photographs are taken or with each image when any change in temperature by more than +/- 0.5 °C.
- Visual images of samples are desired just before and after homogenization (5.2.1) and periodically (see Science Requirements Summary Table, section 5.10.3).
- Need capability to periodically downlink any of the above data.